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ABSTRACT

The use of isoconversional, sometimes called model-free, kinetic analysis methods have recently gained favor in the thermal analysis community. Although these methods are very useful and instructive, the conclusion that model fitting is a poor approach is largely due to improper use of the model fitting approach, such as fitting each heating rate separately. The current paper shows the ability of model fitting to correlate reaction data over very wide time-temperature regimes, including simultaneous fitting of isothermal and constant heating rate data. Recently published data on cellulose pyrolysis by Capart et al. (TCA, 2004) with a combination of an autocatalytic primary reaction and an nth-order char pyrolysis reaction is given as one example. Fits for thermal decomposition of Estane, Viton-A, and Kel-F over very wide ranges of heating rates is also presented. The Kel-F required two parallel reactions—one describing a small, early decomposition process, and a second autocatalytic reaction describing the bulk of pyrolysis. Viton-A and Estane also required two parallel reactions for primary pyrolysis, with the first Viton-A reaction also being a minor, early process. In addition, the yield of residue from these two polymers depends on the heating rate. This is an example of a competitive reaction between volatilization and char formation, which violates the basic tenet of the isoconversional approach and is an example of why it has limitations. Although more complicated models have been used in the literature for this type of process, we described our data well with a simple addition to the standard model in which the char yield is a function of the logarithm of the heating rate.

INTRODUCTION

Much work has been published on polymer decomposition, including numerous kinetic models. Unfortunately, the diversity of polymer formulations, experimental methods, and kinetic analysis methods makes it difficult to obtain from the literature kinetic parameters of the quality needed for quantitative modeling of any given application. The history of kinetic analysis for thermal decomposition has a long and checkered history, which will not be detailed here. Recent debate has centered on a comparison of model fitting methods with isoconversional methods, originated by Friedman (1) and recently popularized by Vyazovkin and Wight (2) as a model-free method. Briefly, isoconversional methods calculate an instantaneous first-order reaction rate constant as a function of reaction extent then determine the activation energy and frequency factor from Arrhenius plots at constant reaction extent.

Due to historical limitations in computing capability, model fitting has traditionally meant fitting a single heating rate experiment, often by mathematically transforming the data to a form that would be linear for any particular model. Vyazovkin and Wight have justifiably criticized this form of model fitting as being unreliable, largely because changes in one or more model parameters away from their true value can compensate for and hide the underlying deficiencies of a particular model. Even though isoconversional kinetic analysis is not model

free in the strictest sense of the term, as when competitive reactions occur, it is usually a pretty good approximation, hence their approach is clearly superior to model fitting of single heating rate data.

A recent report on the ICTAC kinetics project noted that multi-heating rate methods are more reliable than single heating rate methods (3). Even so, most people involved in thermal analysis apparently have missed that it has been readily possible since 1987 to fit models simultaneously to multi-thermal history data sets on personal computers (4). This is accomplished by numerical integration of the model rate equation over the each thermal history and refining the model parameters by simultaneous non-linear regression of all data sets.

Polymers cover a wide range of chemical structures, and their decomposition characteristics are equally diverse. A reaction model we have found (5,6) to be particularly adaptable to a wide range of materials is the extended Prout-Tompkins model

$$d\alpha/dt = k(1-q(1-\alpha))^m(1-\alpha)^n , \qquad (1)$$

where α is the fraction reacted, n is the reaction order, m is a nucleation-growth parameter, and q is an initiation parameter. It has limits of the original Prout-Tompkins model (m=n=1), a first-order reaction, and an nth-order reaction, which is equivalent to a gamma distribution of frequency factors (5). Many polymers show autocatalytic decomposition properties that mimic nucleation-growth characteristics (7). The Prout-Tompkins model is similar in form to a random initiation with short zip length mechanism, and a first-order model is the limit for large zip lengths for either random or end initiation (8).

MATERIALS AND METHODS

Three polymer materials were chosen based on their use in stockpile high explosive formulations (9). Estane 5703 P (Lot 1/97) was obtained in pellet form from the BF Goodrich Co. Kel-F 800 (Lot 553) is a 3:1 copolymer of chlorotrifluorethene and vinylidine fluoride manufactured by 3M Corporation. Viton A, vinylidine fluoride/hexafluoropropylene copolymer (3.5 to 1), was manufactured by DuPont Corporation.

Weight loss measurements of the polymer binders was carried out using a TA Instruments Simultaneous Differential Thermogravimetric Analyzer (SDT), model 2960, manufactured by TA Instruments, using TA open aluminum pans. Approximately 5 mg of material for each sample were decomposed heating rates that ranged from 0.2 to 40 ^{o}C/min from approximately 20 ^{o}C to 550 ^{o}C to provide a broad temperature range for calibration and test of the kinetic model. Degradation was carried out under nitrogen carrier gas at a flow rate of 100 cm^3/min.

The temperature of the SDT apparatus was calibrated at 10 ^{o}C/min using the onset of melting for In, Sn, Pb, and Zn. Calibration at other heating rates found that the temperature error due to heat transfer when using a single heating rate calibration was linear with heating rate. The temperature error was 0.5 ^{o}C or less for all heating rates except 40 ^{o}C/min. Consequently, 1.5 ^{o}C was subtracted from those experiments. Any residual temperature errors would be expected to cause an error in activation energy of ~2 kJ/mol.

Data were collected and processed so that each experiment had between 100 and 1500 points covering the region over which any reaction occurred. Kinetic analysis was done with the LLNL program Kinetics05, which is an upgrade of a program described earlier (5). This program first preprocesses the data using isoconversional kinetic methods to determine general reaction characteristics and initial guesses for nonlinear regression.

CALIBRATION OF KINETIC MODELS

Isoconversional analysis is a simple method to get both a sense of the overall reaction uniformity and an initial estimate of the kinetic parameters. We use the method of Friedman (1), in which the instantaneous rate constant is calculated from the reaction rate and fraction reacted and used in an Arrhenius analysis at constant conversions of 10-90% at 10% intervals. The activation energy as a function of conversion is shown for the three materials in Figure 1. The activation energy at 90% conversion for Viton A has an anomalously high standard error, which is reflective of the breakdown of the isoconversional assumption due to heating-rate-dependent char formation. Otherwise, the activation energies show a gentle slope downward for Kel-F, and gentle slope upwards for Viton A, and a stepped increase at about 40% conversion for Estane. Inspection of the Estane weight loss curve clearly shows the presence of two decomposition processes, with a transition between the two at about 45% conversion.

Another method to get an indication of the average activation energy is Kissinger's method, which uses the shift in T_{max} with heating rate (10). This method gave 186, 216, and 271 kJ/mol, respectively, for Estane, Viton A, and Kel-F. These are within the ranges determined by Friedman's method. An extension of Kissinger's method uses profile width and skewness relative to that expected for a first-order model to determine which reaction model is most appropriate and approximate initial values for non-linear regression (5,6). Since Viton A and Kel-F decompositions are primarily a single reaction, it is easily determined that they have a narrow reaction profile, suggesting a nucleation growth model with values of 0.5 and 0.8 for *m* in eq. 1. Even though Estane has two reaction components, the overall reaction is about as wide as a single first-order reaction, suggesting that each of the two components is also governed by nucleation-growth kinetics.

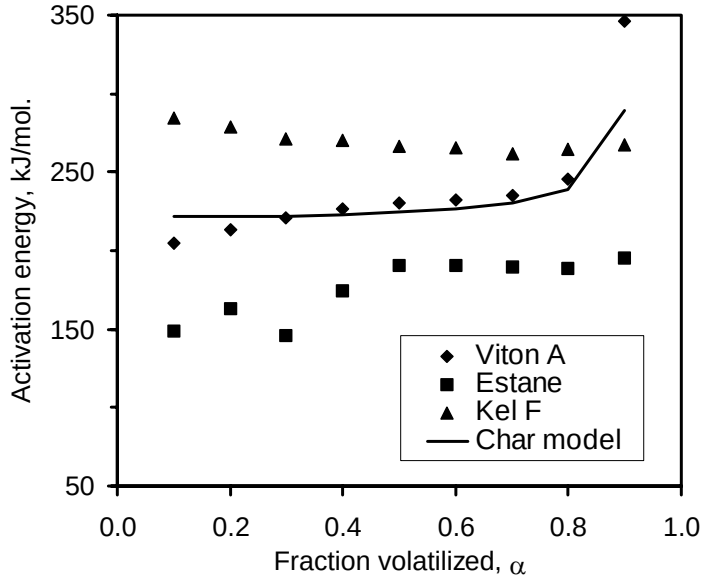

Figure 1. Activation energies derived by Friedman's isocon-versional method. The standard errors for the energies averaged 3.9, 5.8, and 6.4 kJ/mol for Estane, Kel-F, and Viton A, respectively, except that the 90% point of Viton A had an anomalously high standard error of 48 kJ/mol. The solid line comes from analysis of synthetic data with a char yield that depends on heating rate (Table 2).

We used these approximate kinetic analyses in combination with an inspection of the reaction profiles to pick appropriate kinetic models and initial parameter values for model fitting by nonlinear regression. Fitting the models to the fractions converted and reaction rates at all heating rates simultaneously yielded the kinetic parameters in Table 1. Some of the minor parameters were determined manually by inspection. A comparison of measured and calculated reaction extent (fraction of mass lost) is given in Figure 2. The overall agreement is very good over the entire reaction extent and simultaneously matches the shift in profile location with

heating rate. The energies from the non-linear regression agree well the Kissinger values. Also evident in Table 1 is that Viton A has the greatest autocatalytic character (largest value of m). In a separate optimization (not shown), allowing n2 to be optimized for Kel-F resulted in a reaction order of 1.09, with slight shifts in other parameters and negligible improvement in fit.

Table 1. Kinetic parameters determined by nonlinear regression to an extended Prout-Tompkins nucleation growth model, plus minor initial reactions for Viton A and Kel-F and unreactive components for Estane and Viton A.

Parameter	Estane	Viton A	Kel-F
f1	0.420	0.012 (manual)	0.01 (manual)
A1	6.01×10^{10} s^{-1}	1.00×10^{13} s^{-1} (manual)	6.64×10^{12} s^{-1} (manual)
E1	155.0 kJ/mol	167.4 kJ/mol (manual)	146.4 kJ/mol (manual)
m1	0.07	0.0 (fixed)	0.0 (fixed)
n1	1.0 (fixed)	1.0 (fixed)	1.0 (fixed)
f2	0.552	0.960	0.99
A2	1.64×10^{12} s^{-1}	4.74×10^{13} s^{-1}	9.89×10^{17} s^{-1}
E2	183.0 kJ/mol	216.8 kJ/mol	271.3 kJ/mol
m2	0.45	0.77	0.23
n2	1.0 (fixed)	1.0 (fixed)	1.0 (fixed)
f3	0.028 (unreactive)	0.028 (unreactive)	

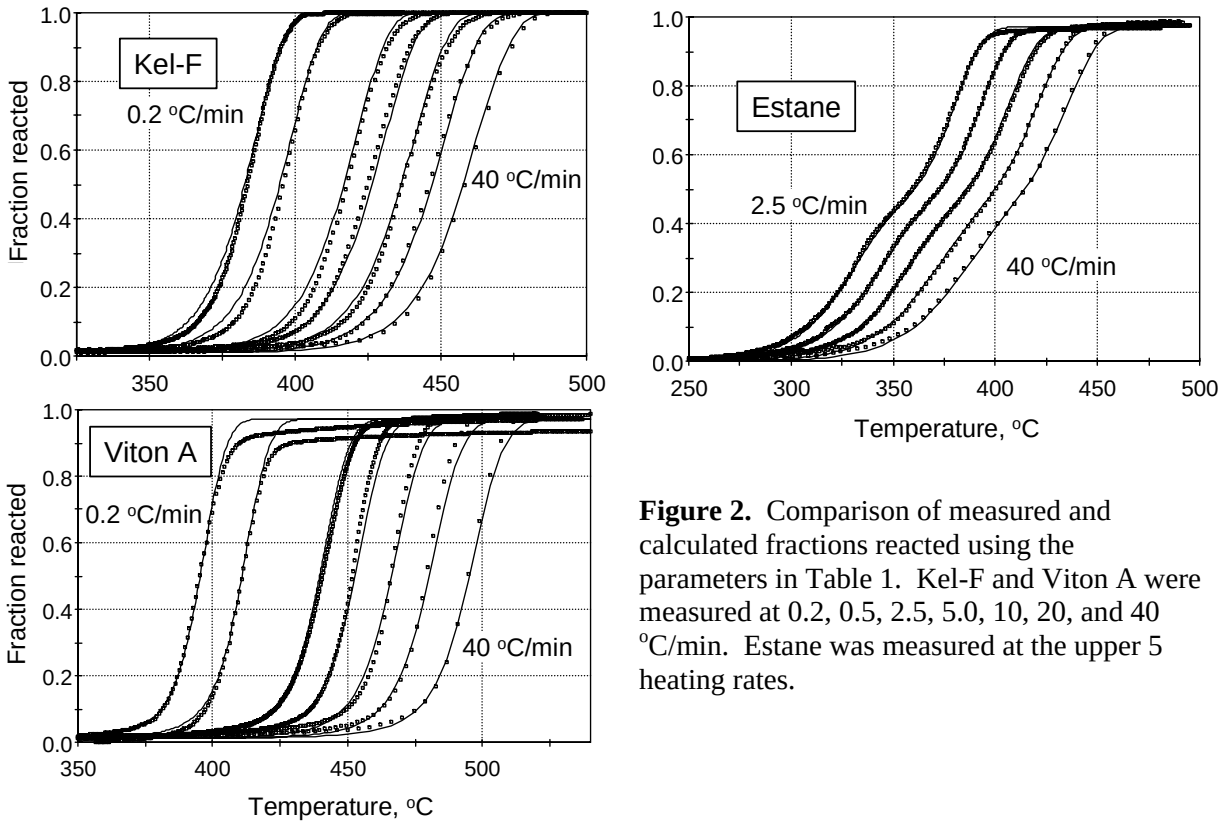

Figure 2. Comparison of measured and calculated fractions reacted using the parameters in Table 1. Kel-F and Viton A were measured at 0.2, 0.5, 2.5, 5.0, 10, 20, and 40 °C/min. Estane was measured at the upper 5 heating rates.

The most obvious deviation between measured and calculated values is the decrease in volatile yield from Viton A as the heating rate is decreased. This is because the increased

residence time of the products at lower heating rates promotes retrograde condensation reactions, yielding coke and gas. Kinetic models are sometimes calibrated in this situation by redefining the maximum yield and renormalizing the conversion data. Alternatively, one can recognize that other systems have found a linear relationship between coke yield and the logarithm of heating rate (11). The coke then undergoes a slower devolatilization characterized by a distribution of reactivity, reflected in either the frequency factor an nth-order reaction or in a distribution of activation energies.

Char yield is a complicated function of sample size, gas flow rate, and other geometric factors that affect the residence time of the pyrolysis products in the sample region. Although we previously developed detailed models for competitive volatilization and retrograde reactions for oil shale (12), we chose the simpler approach of making char formation a simple function of the heating rate according to the relation

$$\text{Fraction of polymer to char} = 0.02 + 0.08\,(1 - e^{-1/Hr}), \qquad (2)$$

where Hr is the heating rate in ^{o}C/min. At low heating rates, $e^{-1/Hr} \rightarrow e^{-\infty}$, which equals zero, so the char yield approaches 10%. At high heating rates, the exponential approaches unity, so the char yield asymptotes to 2%.

The char has sufficient hydrogen that it continues to evolve gas as heated to higher temperatures. Two choices to model that process are an nth-order pyrolysis model for char devolatilization, which would correspond to a Gamma distribution of frequency factors, and a discrete activation-energy distribution model having a finite number of reaction channels. We chose the latter approach, using six reaction channels. The shape of the devolatilization curve above 90% conversion was used to define the distribution of reactivity among the six reaction channels. Not all the char was volatilized. Char typically has an H/C atomic ratio <1, so elimination of hydrocarbon gases (H/C >2) must leave an even more carbon-rich, non-volatile residue.

The resulting model parameters, determined by manual trial and inspection, are given in Table 2. The fraction of original polymer mass is equal to f3 times f3i, and the fraction of original polymer mass remaining at the highest temperature as an unreactive residue is equal to f3 times f_{inert}. A comparison of the model with data for Viton A for conversions greater than 90% is shown in Figure 3. Accounting for the differences in char and ultimate volatile yield causes slight shifts in the Arrhenius parameters for the main reactions, which had been distorted slightly in the previous analysis to partially accommodate aspects of variable char formation and devolatilization.

Synthetic data at 0.2, 2.0 and 20 ^{o}C/min from the model outlined in Table 2 was analyzed by Friedman's method, and the result is shown in Figure 1 along with the original data. The model calculation mimics the upturn in activation at high conversion, although it is not quite as pronounced. The Friedman activation energy at 90% conversion is higher than any of the activation energies in the char devolatilization. This reflects a breakdown in the assumption of the isoconversional model caused by the variable amount of char formed as a function of heating rate, i.e., a competition between two different reaction pathways so that the reactions occurring at fixed conversion are not the same at different heating rates.

Each polymer was pyrolyzed at a fixed temperature to test the ability of the nonisothermal kinetics to predict isothermal behavior. The isothermal temperature was chosen as

Table 2. Kinetic parameters for the extended Prout-Tompkins nucleation growth model, supplemented by a char formation and devolatilization model, for Viton A. Model parameters for reaction components 1 and 2 are denoted by a single index. The double indices for reaction component 3 denote values for each of the six reaction channels.

Parameter	Value	Parameter	Value
f1	0.012 (manual)	f3	$0.02+0.08\times(1-e^{-1/Hr})$
A1	1.00×10^{13} s^{-1} (manual)	A3	1.0×10^{13} s^{-1}
E1	167.4 kJ/mol (manual)	E31	209.2 kJ/mol
m1	0.0 (fixed)	E32	219.7
n1	1.0 (fixed)	E33	230.1
f2	0.988×(1-char fr.)	E34	240.6
A2	7.90×10^{13} s^{-1}	E35	251.0
E2	219.7 kJ/mol	E36	261.5
m2	0.82	f31	0.08
n2	1.0 (fixed)	f32	0.21
		f33	0.18
		f34	0.13
		f35	0.08
		f36	0.05
		f_{inert}	0.27

roughly the 10% conversion point at a heating rate of 2.5 ^{o}C/min so that negligible reaction would occur during heatup at 20 ^{o}C/min, even though Kinetics05 used the exact thermal history to numerically integrate the kinetic equations. The results are shown in Figure 4. The agreement is excellent for Estane and good for the other two polymers. The Kel-F prediction is too slow, while the Viton A prediction is too fast. The discrepancy appears to be related to the estimation of the autocatalytic severity. For the most generally applicable kinetics, the best approach would be to measure isothermal kinetics at one or two additional temperatures and fit the isothermal and constant-heating-rate data simultaneously. The experimental char yield for Viton A agrees well with the model. The model char fraction was chosen as that for a heating rate of 1 ^{o}C/min, which gives a 50% conversion point at approximately the isothermal temperature used here.

COMPARISON TO EARLIER WORK

Our kinetics for Kel-F copolymers agree qualitatively with other published data. The earliest published kinetics on Kel-F appear to be that of Degteva et al.(13,14) They collected products, give Arrhenius plots for a few species, and report an activation energy of 222 kJ/mol—about 20% lower than we obtain. They also observe autocatalytic behavior at their lowest temperature, in agreement with our model. Their data indicates half-lives of 10 hours at 360 ^{o}C and 2 hours at 380 ^{o}C, and our model predicts 6.4 and 1.35 hours, respectively.

David (8) and Wright (15) tabulate pyrolysis kinetics of Kel-F like copolymers of varying monomer ratios. Activation energies ranged from 209 to 285 kJ/mol, which encompass our value. More important, they give rate of 0.06 to 0.18 %/min at 350 ^{o}C. Our expression, being autocatalytic, predicts that the reaction rate increases from an initial value of 0.03 %/min initially (not counting the labile 1%, which would be consumed during sample heatup) to a maximum of 0.07 %/min at 25% conversion. Madorsky (7) also found autocatalytic kinetics for pure poly(chlorotrifluoroethene) and determined an activation energy of 234 kJ/mol, which is slightly lower than our value.

Kinetic results for Viton A in the literature are more varied. David (8) and Wright (15) also report data for Viton A. Activation energies range from 192 to 305 kJ/mol, and the rates at 350 ^{o}C range from 2×10^{-6} to 0.04 %/min. Our calculated rate increases from 0.005 %/min to a maximum rate of 0.05%/min at 42% conversion. Also, we read a maximum rate of mass loss at about 450 ^{o}C at 2 ^{o}C/min in nitrogen from Knight and Wright (16), while we measured 440 ^{o}C.

Cuccuru et al. (17) report a T_{max} of 485 ^{o}C in nitrogen at 10 ^{o}C/min, while obtained 466 ^{o}C. Using single heating rate data, they determine first-order activation energies of 293 and 350 kJ/mol from mass loss and the decomposition endotherm. These are much higher than our values and probably reflect the use of an inappropriate kinetic model, as stressed by Vyazovkin and Wight (2).

Papazian (18) reports TGA analysis of Viton A at 10 ^{o}C/min. He calculates an effective rate constant at each conversion, and then constructs an Arrhenius plot from the single heating rate experiment. He finds that the Arrhenius plot has a break in slope at about 450 ^{o}C, at which point the activation energy changes from 107 to 356 kJ/mol. We do not consider his kinetic analysis method as valid.

There are numerous reports of thermal analysis of various types of polyurethane in the literature (e.g., Grassie and Mendoza (19)), but there are few reports on Estane. Salazar et al. (20) give a detailed description of the same material we have studied. They report an elegant thermal hydrolysis model for Estane, but hydrolysis reactions are different than for our conditions.

The most directly comparable studies are by Singh et al. (21), who report TGA and DSC data for Estane at 10 ^{o}C/min, which also shows a two-step endothermic (320 J/g) decomposition with a shoulder at 350 ^{o}C and peak at 390 ^{o}C. For comparison, we also see the two-step process but with a higher T_{max} at 407 ^{o}C. Their isothermal weight-loss experiments do not show an autocatalytic character. They obtained activation energies ranging from 251 to 261 kJ/mol by fitting a variety of models, presumably to a single heating rate. They also report activation energies as a function of conversion using an isoconversional method, and their figure indicates activation energies of about 175 kJ/mol for conversions less than 0.6 and close to 250 kJ/mol for conversions above 0.8. These are significantly higher than our values.

Calculating isothermal reaction curves for our data and comparing to the data in Figure 5 of Singh et al. (21), we find additional discrepancies. We obtain 90% conversions at 3 and 9 minutes at 390 and 410 ^{o}C, respectively, compared to 12 and 45 minutes estimated from their figure. They do not report frequency factors for their isoconversional analysis, but we can compare to our work using the parameters from their first-order model fit. Their frequency factor of 6.65×10^{16} s^{-1} and activation energy of 252.4 kJ/mol give 90% conversion times in agreement with their isothermal data, but these parameters also give a T_{max} of 428 ^{o}C at 10 ^{o}C/min, which does not agree with either their ramped data or ours. In short, the results of Singh et al (21) are not internally consistent. In contrast, our nonisothermal kinetics agree very well with our isothermal experiment. Even so, we do agree that, although our model has some autocatalytic character in each individual reaction, the composite reaction does not show an acceleratory phase for their high-temperature conditions.

Endres et al. (22) report first-order kinetics for thermal decomposition of polyurethane under thermoplastic processing conditions. However, they characterize reaction extent by the number of bonds broken, as measured by molecular weight, rather than by volatilization. This difference is significant: acceleratory models work for some polymer pyrolysis kinetics because multiple bonds must be broken to form a volatile fragment, and the nucleation growth formalism works as well as or better than a serial reaction model in that case (23).

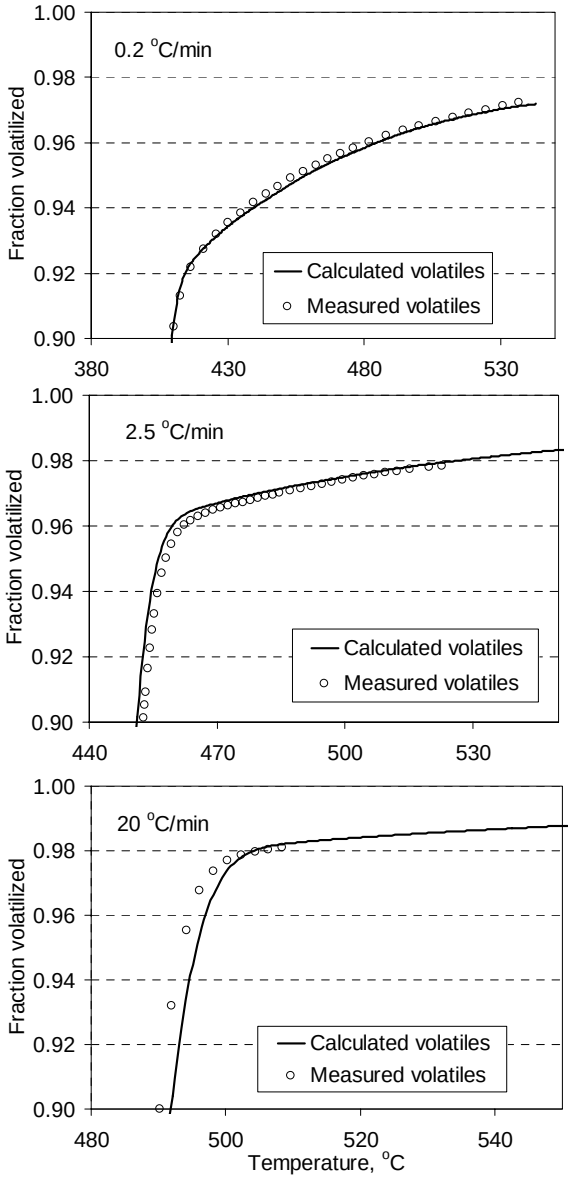

Figure 3. Comparison of measured devolatilization of Viton A with that calculated from the model parameters in Table 2, which include char yield as a function of heating rate and subsequent char devolatilization.

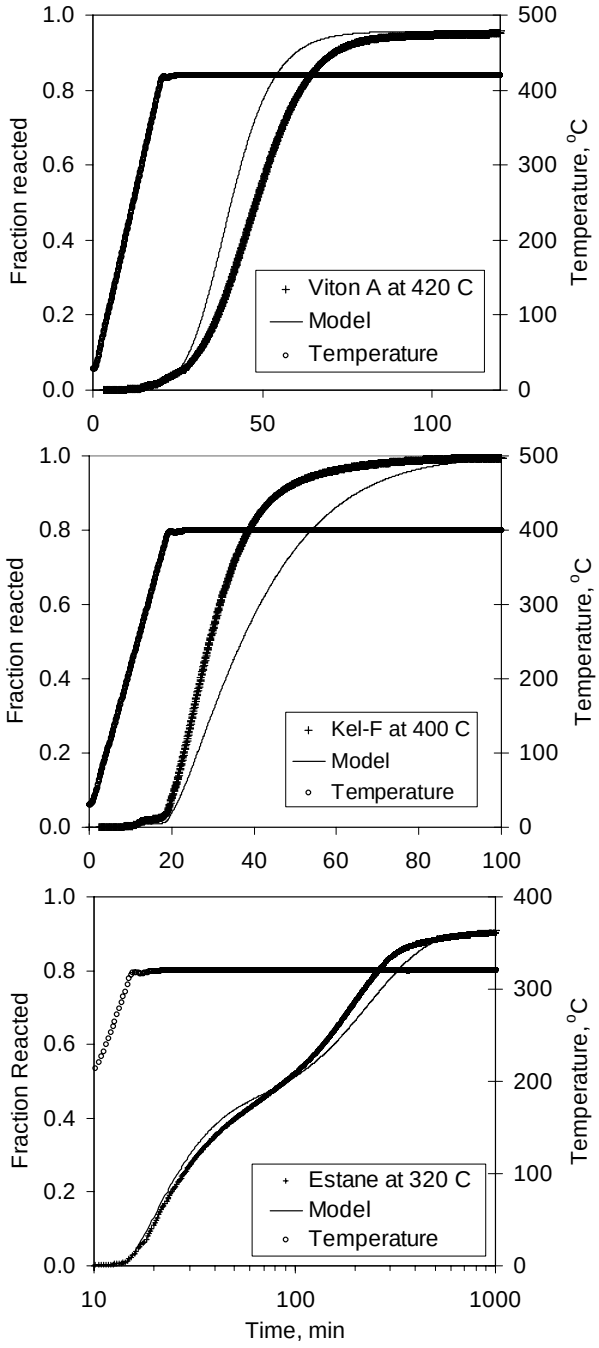

Figure 4. Comparison of measured and calculated fractions reacted for nominally isothermal experiments. The Estane time axis is logarithmic because of the different time scales for the two reactions.

This comparison to the literature indicates that no one to our knowledge has reported kinetic parameters for these polymers based on matching degradation data over a wide range of both conversion and temperature. Most expressions are derived by matching only a few characteristics of the pyrolysis data. Consequently, we view our models as the first that could be used to make detailed predictions of thermal degradation over a wide range of conditions. Although we did not use isothermal data to calibrate the rate expressions in this study, our expressions predict reasonably well the isothermal pyrolysis curves for the single temperatures we explored. The model development methods used here also worked for both isothermal and constant heating rate conditions for cellulose (24), which shares many of the reaction characteristics of these polymers (autocatalytic, some char formation).

CONCLUSIONS

When done properly, model fitting has the ability to derive kinetic models that work over wide range of temperatures and conversions. An absolute requirement for this to work is using either multiple heating rates with a dynamic range of at least ten, or some combination of isothermal and constant heat rate experiments. The three polymers studied here all exhibited autocatalytic behavior, which is typical of linear polymers. This behavior is consistent with either random scission or end initiation with a short zip length. Activation energies derived are consistent with the best previously published work.

Isoconversional kinetic methods work well for most of the pyrolysis but have limitations during the final stages of Viton A and Estane, which form a char whose yield depends on heating rate. The problem was most evident for Viton A, which was studied over a wider heating rate range and therefore had a wider range of char yield. Our multi-heating-rate model-fitting approach was able to fit this char-yield characteristic by making the ratio of immediately volatile products to char a function of the logarithm of the heating rate. The char then undergoes addition devolatilization at higher temperatures, in agreement with experiment.

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